Studies on the Organic Phosphorescence. III. Quenching by Some Gases and Vapors

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Introduction

The preceding investigation[1] on the phosphorescence of trypaflavine-silicagel phosphor has led to a plausible conclusion that there exists a metastable state (M state), which is directly coupled with a triplet state, and it has been proposed that Lewis' scheme must be replaced by the one shown schematically in Fig. 1.

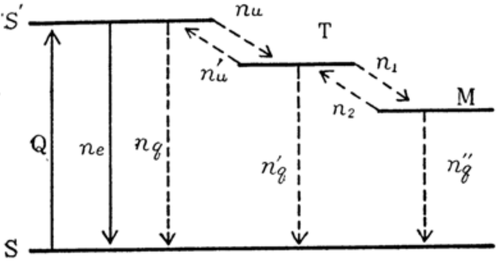

Fig. 1.

On the basis of this mechanism, decay curves are represented by the following equation,

$$I_P = A \exp(-\alpha t) + B \exp(-\beta t) \qquad (1)$$

and putting

$$\pi_1 = n_u'(1 - n_u/\pi) + n_1 + n_q'$$

$$\pi_2 = n_2 + n_q''$$

$$\pi = n_e + n_q + n_u,$$

$\pi_1, \pi_2, n_1 n_2$ and $u_u n_u'/\pi$ are calculated from four parameters ($\alpha, \beta, A/B$ and I_L/I_{P0}) which are obtained from the measurement of I_L (the intensity of luminescence during excitation), I_{P0} (the initial intensity of the phosphorescence) and the decay curve of phosphorescence.

Now, although the existence of another metastable state other than Lewis' triplet state has been established in the preceding paper, nothing as yet is known about its nature.

As a first step to study about it, the author has investigated the influence of the addition of a third substance upon the steady state emission and upon the decay curve of phosphorescence.

Such an investigation is expected, in addition, to refer to our first plan mentioned in the first paper[2] of this series, i. e. the problem whether a third substance (quencher) affects S' or T state, because the analysis of the decay curve makes it possible to evaluate some of the transition probabilities between the states involved in the phosphorescence.

In this paper the influence of some gases and vapors upon the phosphorescence of trypaflavine-silica gel phosphor will be reported. It is well known that such a phosphorescence is effectively quenched by certain gases and especially, a remarkable quenching action of oxygen has been studied from various view points[3], but the precise investigation about the variation of the decay curve caused by the addition of these gases including oxygen, has not yet been undertaken.

Experimental

Materials.—*Trypaflavine-silica gel phosphors* were prepared in the same way as described in the previous paper.

Oxygen and hydrogen were prepared by the electrolysis of baryta water and were first passed over platinized asbestos, then through a dry ice trap.

Nitrogen, argon and methane: The gas from a cylinder was stored for several days, to remove oxygen, in an ampoule the inner surface of which was covered by an evaporated film of metallic sodium.

Nitric oxide was prepared by the reaction between potassium nitrate and ferrous sulfate in the acidified aqueous solution, and then purified by a standard method*.

Other quenchers (*n*-hexane, propylene, benzene, acetone, methanol, SO_2, I_2, ether, dioxane, cyclohexene, 2-ethyl-1-hexene, styrene and methylmethacrylate), after ordinary purification, were distilled or sublimed five times in high vacuum to remove oxygen.

Procedure and Measurement.—A known amount of a gas or a vapor to be investigated was taken in a space between two taps and then

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[1] S. Kato and M. Koizumi, This Bulletin. **30**, 27 (1957).

[2] S. Kato and M. Koizumi, This Bulletin, **27**, 189 (1954).

[3] J. Franck and P. Pringsheim, *J. Chem. Phys.*, **11**, 21 (1943).

* "Inorganic Synthesis", (1939), 11, P. 126.

was introduced into the ampoule containing the phosphor. If there was any fear of even a slight reaction between a gas and tap-grease, the taps were replaced by a mercury cut and a break-seal.

The apparatus used was the same one described in the preceding paper and the phosphorescence of a sample was recorded, before and after introduction of a quencher at 25°C.

In every experiment the greatest caution was paid to eliminate any trace of oxygen and to avoid contamination of a sample with it throughout all procedures. In fact, the disturbance from oxygen is so strong that a noticeable fall of the phosphorescence is observed if the connection tube of the ampoule is carelessly sealed off by fusion.

Results and Discussion

a) General Remarks. — Among the materials examined, argon (38×10^{-5} mol.), nitrogen (43×10^{-5}), hydrogen (32×10^{-5}), methane (42×10^{-5}), *n*-hexane (6.6×10^{-5}), propylene (3.3×10^{-5}), benzene (1.0×10^{-5}), acetone (42×10^{-5}), methanol (3.2×10^{-5}) and water (3.5×10^{-5}) had no effects on a 4 g. phosphor (contained in an ampoule of 20 ml.) of which the dye concentration is 5×10^{-7} mol./g. silica gel; the intensity of the steady state emission and the shape of the decay curve were not affected at all by the introduction of these gases.

When more than 10^{-3} mol. of methanol or water is introduced, the life of the phosphorescence is somewhat shortened and its initial intensity decreases, though only very little. In view of a rather large quantity of a quencher in these cases, it is more plausible to attribute these effects to the variation in the property of gel, hence these cases will be omitted from the discussion given below.

The substances which show more or less positive effects are O_2, NO, SO_2, I_2, ether, dioxane, cyclohexene, 2-ethyl-1-hexene, styrene and methyl methacrylate.

When a suitable amount of a quencher listed above, is introduced, the phosphorescence intensity, the decay constant as well as the intensity of the steady state emission show measurable changes. Decay curves are still represented by equation (1) unless the quantity of a quencher is not too large. When it exceeds a certain value, equation (1) must be replaced by a more general one

$$I_P=\sum a_i \exp(-\alpha_i t) \qquad (2)$$

in order to represent the decay curve satisfactorily. But even in these cases, the decay curves are exactly the same in shape for different intensities of the exciting light, so it is certain that no process of higher kinetic order is involved in the phosphorescence phenomenon.

TABLE I

Sample Dye conc.		Quencher mol.	I_L	I_L/I_{P0}	$I_L^0/(I_L^0-I_L^q)$
0.43 μmol./g.	4 g.	None	100	2.88	2.86
		O_2 : 1.26×10^{-8}	65	—	
0.5 μmol./g.	4.2 g.	None	100	2.59	2.63
		Styrene : 2.63×10^{-5}	62	—	

TABLE II

Phosphor: 0.5 μmol./g., 4 g.; 25°C. Time unit is second.

No.	Quencher mol.	α	β	A/B	I_L/I_{P0}	π_1	π_2	n_1n_2	n_un_u'/π
1	None	2.02	5.6	0.79	2.77	4.8	2.8	2.2	5.2
	O_2 : 1.5×10^{-10}	4.35	12.3	0.54	4.3	11.0	5.6	8.3	4.1
2	None	1.60	5.2	0.62	2.59	4.8	2.2	1.8	2.4
	O_3 : 7.5×10^{-10}	4.49	30	0.32	8.72	29	5.7	28	3.0
3	None	1.77	6.2	0.74	2.66	5.4	2.5	2.8	2.6
	NO : 1.2×10^{-9}	4.42	19	0.45	13.2	18	5.8	18	1.2
4	None	1.68	6.2	0.57	2.60	5.5	2.3	2.4	2.8
	Styrene : 1.2×10^{-6}	3.54	12.7	0.49	7.53	12	4.7	9.2	1.5
5	None	1.58	5.3	0.74	2.94	4.6	2.2	1.9	1.9
	Ether : 6.9×10^{-6}	2.82	8.0	0.51	3.67	7.2	3.6	4.4	1.8
6	None	1.42	5.0	0.68	2.92	4.4	2.0	1.7	1.9
	Dioxane : 3.0×10^{-5}	3.46	16	0.36	6.32	15	4.4	11.0	2.3
7	None	2.52	8.0	0.88	2.57	6.8	2.7	5.0	3.5
	SO_2 : 2.6×10^{-6}	6.27	16	1.31	3.94	13	9.6	21	3.6

b) Effect of Quenchers on I_L. — When a suitable amount of gas depending on its quenching efficiency is introduced, the phosphorescence is completely quenched and an interesting relation in the form of (3) is found to hold. Thus, rewriting I_L before and after the addition of a quencher as I_L^0 and I_L^q respectively and denoting the initial phosphorescence intensity as I_{P0}^0 and I_{P0}^q respectively for the corresponding case*,

$$I_L^0/(I_L^0-I_L^q)=I_L^0/I_{P0}^0. \tag{3}$$

From (3)

$$I_L^0-I_L^q=I_{P0}^0$$

or

$$I_L^q=I_L^0-I_{P0}^0=I_F^0. \tag{4}$$

Since $I_{P0}^q=0,\ I_F^q=I_F^0.$ (5)

Equation (5) shows that in such a favorable condition, phosphorescence is completely quenched and yet a pure fluorescence is not affected at all.

I_F is the luminescence emitted by molecules which after having been excited to S′ state, drop to the ground state directly without going to T or M state. Therefore, it can be concluded that in such a case S′ state is not affected at all by a quenching gas. A few examples are shown in Table I.

For other quenchers the same relation holds, hence it is quite certain in general, that under the situation that the phosphorescence is partially quenched, the quencher does never affect S′ state and the intensity of pure fluorescence remains constant.

c) Analysis of Decay Curves. — Decay curves were taken for the same sample with and without a quencher; usually when a quenching gas was removed by evacuation the sample regained exactly the same decay curve as that of the original one. Results of the analysis are shown in Table II, where the data for a quenched sample is paired with them for a reference. The data for each reference sample do not always coincide, probably because of some difference in the pretreatment of the sample or in the source of silica gel.

Here it is to be noted that although the values of α and I_L/I_{P0} are rather accurately obtained, those for β, and A/B are not so accurate; probable errors for the latter two quantities would usually be ±10% or so. Hence accuracy for π_1, π_2, n_1n_2, n_un_u'/π is much worse than this.

It is seen from the table that π_1, π_2 and n_1n_2 are increased much by the introduction of a quenching gas, while n_un_u'/π in most cases are not affected beyond probable error. From the latter result, it can be concluded that n_u', the transition probability from T to S′ is not affected by a quencher, because, as already established in the preceding section, π and n_u must remain constant in the present conditions.

This result may perhaps support the view that the transition from the lower state to the higher state is in general not promoted by such a perturbation as is due to spin orbital interaction.

It is noteworthy that the quenching gases not only induce the emissionless transitions from T to S and perhaps M to S, but they also increase the transition probability between T and M.

Judging from the relation

$$\frac{I_F}{I_{P0}}=\frac{I_l-I_{P0}}{I_{P0}}=\frac{\pi\alpha\beta}{n_un_u'\pi_2}=\frac{\pi}{n_un_u'}\left(\pi_1-\frac{n_1n_2}{\pi_2}\right),$$

the decrease in the initial intensity of phosphorescence is mainly due to the increase of π_1 value, since this is usually much greater than that of n_1n_2/π_2. Thus broadly speaking, quenching action of the gaseous substances comes from their attack on T state.

Next it is worthy to note that the quantities of quenchers are, in some cases, exceedingly small compared with that of the dye. For example, the quantity of oxygen or nitric oxide which is required to cause a measurable quenching is of the order of 10^{-10} mol. as against 2×10^{-6} mol. of dye. Consequently it is clear that one oxygen or nitric oxide molecule acts as an effective quencher towards more than one thousand molecules of dye. Hence it may safely be concluded that the quenching action of these substances is not of static type but of kinetic or collisional one.

In other quenchers, styrene etc., the quantities are comparable to that of the dye. In spite of such great differences in quantity, the general features of quenching are similar at least qualitatively, no specificity being observed in most quenchers. It seems, however, that SO_2 is an exception, since the increase of n_1n_2 and π_2 is abnormally high compared with other cases. The problem would be worthy of further study.

d) Effect of Oxygen on the Pure

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* Throughout this paper analogous notations will be used for all the other constants. For example, π_1, which will still be used in general case, will be replaced by $\pi^0{}_1$ and $\pi_1{}^q$ when the distinction is necessary.

Fluorescence.—As described above, only phosphorescence is quenched by a very small amount of oxygen, but a much larger quantity of it quenches the fluorescence too to some extent. Some examples are shown in Table III.

TABLE III

O_2 press. in mmHg	<0.1	10	30	100	720
I_L	100	87	74	50	2

In the experiment at <0.1 mm O_2 press., fluorescence keeps its full intensity while phosphorescence is completely quenched, so that I_L in this case is equal to the intensity of pure fluorescence I_F when the quencher is absent. Other data for I_L, accordingly, are the values of $I^q{}_F$. Now the volume of the ampoule, used for the quenching experiment of phosphorescence is about 20 ml., therefore, 10^{-10} mol. of oxygen corresponds to 10^{-4} mmHg under the assumption that oxygen is not adsorbed on silica gel at all. Thus the quenching constant for the phosphorescence is estimated to be roughly of the order more than 10^6 times greater than that for fluorescence. The lifetime of S′ state, on the other hand, being of the order 10^{-7}–10^{-9} sec., is 10^6–10^8 times shorter than that of T or M state. Thus it appears that the great difference in the behavior of T state against S′ state when oxygen is introduced, is mainly due to its long lifetime and not due to its intrinsic reactivity.

e) **Another Evidence for the Present Scheme of Phosphorescence.** — Although the present scheme of phosphorescence has been supported to some extent in the preceding paper, here another evidence will be added which can be derived from the above quenching experiments.

As already described[2)], if phosphorescence obeys Lewis' mechanism and a quencher only acts on T state, promoting only the emissionless transition to the ground state, then the initial intensity of phosphorescence must be exactly proportional to the lifetime.

Now, according to the present investigation, S′ state is not affected at all when the phosphorescence is partially quenched. Therefore, if the phosphorescence consisted of two independent ones, the product of the decay constant and the initial intensity should be unchanged for each independent process when a quenching gas is introduced. In other words, $A\alpha$ and $B\beta$ should be constant and accordingly the product $A/B\times\alpha/\beta$ should also be unaffected. This conflicts with the data given in Table II.

Some examples are shown in the following Table.

TABLE IV

	Quencher	$A/B\times\alpha/\beta$
No. 1	None	0.28
	O_2 1.5×10^{-10} mol.	0.19
No. 2	None	0.19
	O_2 7.5×10^{-10} mol.	0.05
No. 3	None	0.2
	NO 1.2×10^{-9} mol.	0.1

Thus the existence of any two independent phosphorescence processes is not compatible with the above results, unless the transition probability from T to S′ is notably increased by a quenching molecule; this increase appears to be very improbable.

Summary

The quenching action of some gases and vapors upon the phosphorescence of silica gel-trypaflavine phosphor was investigated. The gases which have more or less quenching effects are $O_2>NO>SO_2$, styrene> ether, dioxane, cyclohexene, 2-ethyl-1-hexene, methyl methacrylate, and the gases with no effects (when the quantities are not too large) are N_2, Ar, H_2, methane, *n*-hexane, propyrene, benzene, acetone, methanol and water.

The influence of quenching gases on the decay curve of phosphorescence were accurately examined and by analysing them on the basis of the scheme proposed in the preceding paper, it was established that in general S′ is not affected while both T and M state are appreciably affected. Furthermore, it was found that T→S′ transition is not promoted in general.

The quenching actions of O_2 and NO were interpreted to be of kinetic type.

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